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IODINATION OF AROMATIC COMPOUNDS USING IODINE AND M-CPBA

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ABSTRACT

An efficient and straightforward method for iodination of aromatic compounds is reported using I_2 and mCPBA. Iodine and mCPBA are used to generate electrophilic substitutions of iodine. Nomineral acid was used in this reaction. This method is simple and no column purification is required.

KEYWORDS: Iodine, mCPBA, Aromatic Compounds, Iodination & Regioselectivity

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Original Article

INTRODUCTION

Many cross coupling reactions in organic chemistry requires aryl iodides as important synthetic building blocks. These compounds are mainly used in the generation of carbon–carbon and carbon–nitrogenw bond formation and in cross coupling reactions [1]. In general, direct iodination on aromatics compounds was done by using Lewis acid and oxidizing agent. However, the direct iodination is difficult due to low electrophilicity of I+ compare to chlorides and bromides. Recently, a variety of iodinating agents have been reported for direct and regioselective iodination which includes HgO-I_2 [2], trichloroisocyanuric acid / Iodine/ Silica [3], Iodine-periodic acid [4], C_5H_5NICl [5], NH_4I-H_2O_2 [6], $I_2/O_2/H_5PV_2Mo_{10}O_{40}$ [7], and other reagents [7-14]. There are several issues related to the above-mentioned methods. To overcome these issues using our past experience [15-20]ported a simple method for the synthesis of iodination of aromatics using I_2-mCPBA in acetic acid.

EXPERIMENTAL METHODS

General Experimental Procedure

In a clean RBFaromatic compound (1 mmol.), Iodine (1 mmol.) in DCM (10 ml) were added Acetic acid (2 mL) and mCPBA (1.1 mmol) at room temperature. After the starting material consumption, the reaction was washed with an aqueous Na2S2O3 solution and extracted with DCM. The organic layer on evaporation under reduced pressure to get pure compound. Few of the synthesized compounds were confirmed and their analytical data was given below.

Compound 2a

Yield: 87 %, Melting point131-133˚C , FTIR(KBr,cm- 1): 3445,1681,1244, 593, ^{1}H NMR (Chloroform-D_3,500 MHz): δ ppm2.83 (3H, s),7.24–8.02 (3H, m),13.85 (1H, s), ^{13}C NMR (Chloroform-D_3,125 MHz): δ ppm34.2, 87.8, 119.2, 122.6, 137.6, 143.5, 161.5, 202.5, Anal.Calc for $C_8H_7O_2I$,%:C 36.67;H 2.68;I 48.44.Found: C 36.71;H. 2.74;I. 48.50.

Compound 2b

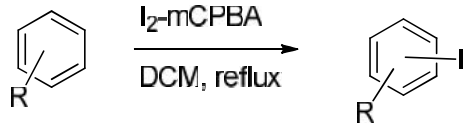
Yield: 85%, Melting point 155-159˚C, FTIR(KBr, cm- 1): 3436,1694,1249, 583, ^{1}H NMR (Chloroform-D_3,, 400 MHz):δ 2.6(s,3H),6.9–8.0 (m,3H), 8.5 (s, 1H), ^{13}C NMR ($CDCl_3$,100 MHz, δ / ppm): 35.4, 88.4, 115.3, 122.5, 123.4, 137.1, 155.2, 197.5, Anal.Calc for $C_8H_7O_2I$,%:C 36.67;H 2.70;I 48.42.Found: C 36.68;H 2.69;I 48.48.

Compound 2c.

Yield: 84 %, Melting point 161-164˚C, FTIR(KBr, cm- 1): 3417,1699,1254, 573, ^{1}H NMR (Chloroform-D_3,500 MHz): 2.7 (s,3H),7.2–8.0(d,4H), 8.5(s, 1H), ^{13}C NMR (Chloroform-D_3,125 MHz):δ 34.3, 88.8, 118.9, 129.2, 134.2, 139.5, 160.4, 198.2, Anal.Calc for $C_8H_7O_2I$,%:C. 36.68;H. 2.68;I. 48.45.Found: C. 36.69;H. 2.68;I. 48.46.

RESULTS AND DISCUSSIONS

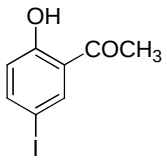
In this method, arenes were iodinated using iodine with mCPBA in aqueous CH_3COOH. The I+ electrophile is created by I_2-mCPBA reaction in acetic acid. the formed iodinating reagent reacts with aromatic compound to form mono substituted iodocompound. It is a high regioselective reaction and only mono-iodination has occurred. When the substitution on aromatic moiety is –OH $–CH_3$, $-NH_2$and —OCH_3, (entries d, h, j and l) iodination will happen at *para position only*. In this method, the reaction is simple, shorter time and give good yield (74–88%, Table 1). The structures of the synthesized compounds were mentioned in the below table.



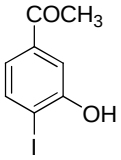
R= NH_2, OH, OCH_3, CHO, CH_3, $COCH_3$
H,Cl,Br, OCH_3, NO_2

Scheme 1: Aromatic Compounds Iodination

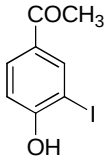
Table 1: Iodination of Aromatic Compounds



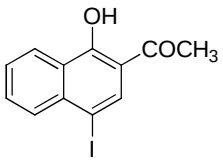
2a, 88%



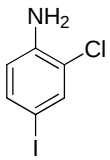
2b, 84%



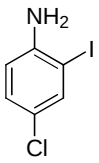
2c, 88%



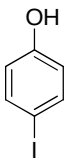
2d, 86%



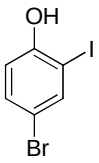
2e, 79%



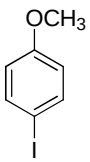
2f, 74%



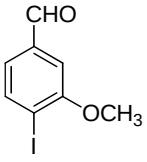
2g, 84%



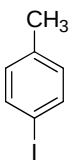
2h, 80%



2i, 82%



2j, 74%



2k, 82%

CONCLUSIONS

In conclusion, we have reported a facile iodination of aromatic compounds using I_2 and mCPBA was reported with good yields and higher chemo selectivity. All the reactions were well tolerated and yielded the desired iodine product with good yields. In addition, this method is having easy work-up, less time of reaction and high yields without any further purification.

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